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54 **Process for the selective hydrogenation of triglyceride oils and products so obtained.**

57 Triglyceride oils, which contain besides fatty acids having two double bonds, fatty acids having more than two double bonds, are hydrogenated using palladium, platinum, rhodium and/or iridium as a catalyst, the catalyst being treated with dry ammonia. The hydrogenation is carried out at a temperature of at least 100°C. The hydrogenation progresses in a particularly selective manner. On using, for instance, soya-bean oil, which contains about 65% of linoleic acid and 7% of linolenic acid, the amount of linolenic acid can be reduced to 2%, whereby more than 45% of linoleic acid is retained in the hydrogenated product. In case the catalyst is not treated, said amount is only about 35%.

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PROCESS FOR THE SELECTIVE HYDROGENATION OF TRIGLYCERIDE OILS WITH A METALLIC CATALYST IN THE PRESENCE OF AMMONIA

The invention relates to a process for the selective hydrogenation of unsaturated fatty acid derivatives, such as triglycerides, which contain besides fatty acids with two double bonds, fatty acids with more than two double bonds.

5

As is generally known, oils and fats consist mainly of a mixture of triglycerides of fatty acids. The fatty acids usually contain about 16 to about 22 carbon atoms and may be saturated, e.g. stearic acid; mono-unsaturated, e.g. oleic acid; di-unsaturated, e.g. linoleic acid; or tri-unsaturated, e.g. linolenic acid, or may even be unsaturated to a greater degree.

In the field of technology relating to oils and fats it is usual to hydrogenate oils in order to remove the unsaturation partly, a hydrogenated oil being obtained having the desired properties, such as a higher melting point and/or increased stability.

During the hydrogenation a number of reactions take place, both successively and simultaneously. Accordingly, for example, in the hydrogenation of linolenic acid the hydrogenation reactions can be represented by the following simplified scheme:

linolenic acid  $\xrightarrow{K_1}$  linoleic acid  $\xrightarrow{K_2}$  oleic acid  $\xrightarrow{K_3}$  stearic acid,  
the rate constants of the reactions being indicated with  $K_1$ ,  $K_2$ , etc.  
Moreover, side reactions occur, such as displacement and isomerisation of double bonds. Isomerisation gives rise to the conversion of cis-double bonds into trans-double bonds, the corresponding oils which contain the trans-acids usually having a higher melting point. Oils and fats which have a high content of stearic acid have a melting point that for most applications is too high to be organoleptically acceptable. Formerly it was therefore usual to direct the hydrogenation in such a way that as little stearic acid was formed as possible, but that still a high content of trans-oleic acid was obtained, so that the oil had the desired melting point. Nowadays it is considered less desirable to apply cis-trans iso-

merisation since there is a shift to liquid, though stable oils, which are used as such or serve as ingredient for soft margarines which are stored in the refrigerator.

- 5 The selectivity values of the hydrogenation reactions are usually defined as follows:

$$S_I = \frac{K_2}{K_3} \qquad S_{II} = \frac{K_1}{K_2}$$

- 10 When the  $S_I$  value of the reaction is high, small amounts of saturated acids are obtained. With a high  $S_{II}$  value it is possible to hydrogenate linolenic acid and still retain a high percentage of the essential fatty acid: linoleic acid. With the isomerisation-selectivity value, abbreviated to  $S_i$ , the amount of trans-isomers is  
15 indicated that is formed in relation to the degree of hydrogenation. As was already observed, it is wanted at present that the hydrogenation be influenced in such a way that the  $S_i$  value is as low as possible.

- 20 However, according to the current practice with hydrogenation, that is usually carried out at a high temperature and under elevated pressure with the aid of a nickel catalyst supported on a carrier, a not unimportant isomerisation of double bonds cannot be avoided.

- 25 The use of some catalysts, for example copper catalysts, has been proposed on account of their higher selectivity. Although it is true that such catalysts are more selective, the degree of isomerisation they bring about is, however, about the same as that of nickel.

- 30 The use of palladium catalysts has been proposed for the selective hydrogenation of soyabean oil (Belgian patent specification 851,202. Although these catalysts are selective, the content of linoleic acid obtained with them is not higher than 40% at a linolenic  
35 acid content of 2% when a soyabean oil containing 7-9% of linolenic acid and 50-55% of linoleic acid is used as starting material.

According to Belgian patent specification 872,476 triglyceride oils are hydrogenated with the aid of a nickel catalyst which has been

treated with a basic nitrogen compound, including ammonia, the molar ratio of nitrogen:nickel being about 0.05-0.4:1.

5 According to Belgian patent specification 872,477 the hydrogenation of triglyceride oils is carried out by means of a nickel catalyst in the presence of a basic nitrogen compound, in which the molar ratio of nitrogen:nickel is about 0.05-0.4:1.

10 According to the last two patent specifications the hydrogenation is carried out at a temperature of 100 to 175°C. Also according to the last two processes in the hydrogenation of soya oil to a linolenic acid content of 2%, linoleic acid contents are obtained lower than 40%, the transisomer content in the hydrogenated product being about 15 to 20%.

15 It has now been found, surprisingly, that with the hydrogenation of triglyceride oils with the aid of metallic catalysts an excellent selectivity and very low trans-contents are obtained when ammonia is present during hydrogenation.

20 The invention is therefore concerned with a process for the selective hydrogenation of unsaturated fatty acid derivatives which contain, besides fatty acids having two double bonds fatty acids having more than two double bonds, in the presence of a catalytically  
25 active metal of group VIII of the periodic system of the elements that as a promotor can contain a metal of the same or another group of the periodic system, and has been treated with a nitrogen compound, which process is characterized in that as the catalytically active metal palladium, platinum, rhodium or iridium is used which  
30 has been treated with dry ammonia in a molar ratio of ammonia to metal of at least 100:1, and hydrogenation is carried out at a temperature ranging from -20° to 100°C.

35 From a technical point of view, the process according to the invention has important advantages, because it can be carried out very simply, ammonia is a very easily obtainable and cheap substance and can very easily be removed from the hydrogenated oil.

It has now been found that with the process according to the invention the hydrogenation is influenced in such a way that a selective hydrogenation of polyunsaturated fatty acid groups takes place without any formation of saturated fatty acid groups at all, while relatively few trans-isomers are formed. Moreover, the invention is characterized in that linolenic acid groups (or trienoic acid groups), if present, are hydrogenated more readily than dienoic acid (linoleic acid) groups with the result that products are formed which have a low content of linolenic acid and a high content of linoleic acid.

As the catalytically active metals, of which palladium and platinum are preferred, also alloys of these metals may be used. Such catalytically active metals may contain promoters, i.e., metals that promote the effect of the catalyst with respect to its activity and/or selectivity, such as Cu, Ag, Au, Zn, Sn, Ti, Hf, V, Nb, Ta, Zr, Cr, Mo, W or Mn.

The catalyst can be used in the form of a porous metal supported on a carrier in sheet-form that is immersed in the system, or preferably in the form of small particles, such as palladium powder, suspended in the system, or a metal sol obtained by reduction of a soluble compound of the metal with a reducing organo-metallic compound. The metallic component can be supported on a carrier. Carbon, silicon dioxide, aluminium dioxide, kieselguhr or an ion-exchange resin can, for example, be used as carrier for the catalyst.

The amount of catalytically active material used for the hydrogenation is not critical and can vary from 1 mg/kg to 10 g/kg, calculated on the basis of the metal with respect to the compound to be hydrogenated, as this amount is dependent on the form of the catalyst, whether supported on a carrier or not, on the specific surface area of the catalyst, on the catalytic activity of the metal used, on the amount of ammonia added, and on other factors.

The activity, selectivity and the formation of trans-isomers effected during hydrogenation with the addition of a certain

amount of ammonia are dependent on the amount of the type of catalyst. When a triglyceride oil is hydrogenated, the quality of the oil and the refining process of the crude oil influence the hydrogenation characteristics when different amounts of ammonia are added.

5

The amount of ammonia to be added should at least be such that the molar ratio to the metal component of the catalyst is at least about 100:1 to achieve an adequate selectivity, i.e. that in the hydrogenation of an oil which contains besides fatty acids having two double bonds, fatty acids having more than two double bonds, an amount of at least 75% of the original fatty acids having two double bonds is retained. In general, these essential fatty acids are retained in an amount exceeding 80%, more often even exceeding 90%.

15

When the amount of ammonia is increased, the selectivity of the hydrogenation is enhanced, although on further increasing said amount, the effect will gradually decrease. At molar ratios of ammonia to catalytically active metal greater than about 2,000:1, no improvement is noticeable. However, larger amounts are not detrimental and the above-mentioned molar ratio may be 5,000:1 and above.

20

In carrying out the process of the invention the compound to be hydrogenated can be dissolved or dispersed in an organic liquid, such as a hydrocarbon, e.g. hexane, or a ketone. Good results are also obtained with alcohols, but in that case alcoholysis or esterification can take place; when alcoholysis or esterification is desirable, alcohols can therefore also be used.

25

The ratio of liquid to substrate is not critical and is usually not greater than about 20:1.

30

The hydrogenation can also be carried out in the pure compound.

35

Generally the hydrogenation is carried out in a suitable apparatus, such as a reaction vessel with a stirrer, or continuously in a series of reaction vessels with stirrer, though good results can also be obtained when the hydrogenation takes place over a column of



catalyst particles.

5 The hydrogenation can be carried out by suspending the catalyst in the solvent, when this is used, under hydrogen, and to pass gaseous ammonia through the suspension for some time, for example for 1 to 10 minutes. Optionally the treated catalyst can now be isolated and be added to the substrate to be hydrogenated. The hydrogenation can also be started by adding the substrate to be hydrogenated and the hydrogen subsequently to the treated suspension. When the ammonia  
10 is introduced, the catalyst can also be suspended in the substrate to be hydrogenated or in a solution of the substrate in the solvent. The hydrogen gas, which is used for the hydrogenation, can also contain ammonia. Finally it is also possible to treat the catalyst first with liquid ammonia.

15

The temperature at which hydrogenation is carried out should be at least 100°C. Good results with active catalysts were obtained at temperatures from -20°C, particularly at 10°C to 60°C.

20

The reaction can be carried out under atmospheric pressure or under higher pressure; generally the pressure will vary from 100 to 2500 kPa. Naturally, if it is desired to work at a temperature above the boiling point of any liquid used, a pressure above atmospheric pressure should be applied.

25

The process can be regulated in a known manner, for example by stopping the hydrogenation when a previously calculated amount of hydrogen has been absorbed.

30

The process according to the invention can be applied for the hydrogenation of compounds or groups which contain more than one double bond in order to increase the selectivity of the hydrogenation reaction. Examples that can be mentioned are the hydrogenation of soybean oil, rapeseed oil, linseed oil, fish

35

oils, tallow and similar animal fats, palm oil, esters of fatty acids, such as the methyl-, ethyl- and other alkylesters, soaps, alcohols and other fatty acid derivatives in which hydrogenation plays an important part.

The products can be used as deep-frying oil, table oil, as raw material for margarine or as raw material for the preparation of stable products such as soaps, esters, etc.

- 5 The invention is further illustrated by means of the following Examples. In some Examples the sum of the amounts of components does not add up to 100%, as less important fatty acid components, such as C<sub>14</sub>-, C<sub>17</sub>-, C<sub>20</sub>- and C<sub>22</sub>-fatty acids, are not mentioned. The composition of the substrates before and after hydrogenation is  
10 given in mol.%. Other percentages are calculated by weight.

- In the Tables the fatty acids are designated by the number of carbon atoms present therein and the number of double bonds, that is to say C18:3 means linolenic acid and isomers, C18:2 means  
15 linoleic acid and isomers, etc.

#### Example 1

- The hydrogenation was carried out under atmospheric pressure and at room temperature in an apparatus consisting of a vessel with a  
20 net volume of 100 cm<sup>3</sup> and provided with a magnetic stirrer, four baffle plates, an inlet for hydrogen, an inlet for substrate and a device for drawing off samples.

- The reactor was connected with a 500 cm<sup>3</sup> calibrated burette filled with hydrogen (purified over a copper catalyst (BTS) and a molecular  
25 sieve and paraffin oil).

- The reactor was loaded with 60 g palladium on carbon (3%) and 70 cm<sup>3</sup> acetone. The reactor was repeatedly degassed and filled  
30 with hydrogen. The solution was stirred and after 15 minutes water-free ammonia was slowly bubbled through the solution for 5 minutes. Subsequently soyabean oil was added to the reactor and the hydrogenation was started.

- 35 At fixed intervals samples were drawn off for determination of the fatty acid composition by GLC and the trans-content by IR, as is shown in Table I. After the hydrogenation the ammonia concentration was determined by potentiometric titration with alcoholic HCL



(in the present case 0.3N  $\text{NH}_3$ ).

TABLE I

Hydrogenation time (min.)	Fatty acid composition (mol.%)					Trans (mol.%)
	C16:0	C18:0	C18:1	C18:2	C18:3	
Starting oil	10.6	3.6	23.3	55.7	6.6	< 1
40	10.7	3.7	30.2	52.7	2.8	5
57	10.6	3.6	32.9	52.0	1.9	7
81	10.5	4.0	37.3	46.8	1.4	8

In a comparative test in which no ammonia was used, but otherwise under the same conditions, the following result was obtained:

15

Hydrogenation time (min.)	Fatty acid composition (mol.%)					Trans (mol.%)
	C16:0	C18:0	C18:1	C18:2	C18:3	
12	10.7	5.0	46.5	35.5	2.0	12

20

Example 2

Example 1 was repeated, with the exception that other solvents were used instead of acetone and sometimes another amount of catalyst, as is indicated in Table II. The fatty acid composition at 2% C18:3 was determined by interpolation.

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TABLE II

Selective catalytic hydrogenation of soyabean oil ( $\leq 5$  g) in various media ( $70\text{ cm}^3$ ) with 60 mg Pd/C as catalyst and water-free ammonia as additive.

Solvent	Pd/C (mg)	NH <sub>3</sub> (m <sup>3</sup> )	Fatty acid composition (mol.%)					Trans (mol.%)	Reaction time (min.)
			C16:0	C18:0	C18:1	C18:2	C18:3		
Starting oil			10.6	3.6	23.3	55.7	6.6	< 1	
Dimethyl formamide (DMF)	60	0.3	10.7	3.5	30.9	52.9	1.7	6	100
Ethyl acetate	60	0.5	10.2	3.4	33.5	50.8	2.0	8	150
Isopropanol	60	1.5	10.6	3.6	33.1	50.5	2.0	6	100
Hexane	60	0.1	10.7	3.6	35.1	48.6	2.0	7	180
Diglyme	100	0.5	10.5	3.7	29.6	54.0	2.1	9	55
Tetrahydrofuran (THF)	160	0.15	10.4	3.7	34.3	49.6	2.0	7	57

Example 3

An investigation was made as to the effect of the amount of ammonia on the hydrogenation behaviour of soyabean oil.

- 5 In this Example a 1 dm<sup>3</sup> autoclave was used which was provided with a heating spiral through which thermostated water could be passed, a stirrer, an inlet for gases, a sampling device and a manometer.

- 10 Soyabean oil was hydrogenated in the autoclave at a temperature of 25°C and a pressure of up to 500 kPa. In each experiment of the Example the autoclave was charged with 100 mg palladium per kg of oil of a 5% palladium-on-carbon catalyst, 250 ml of soyabean oil and 250 ml hexane. The reactor was degassed two or three times, flushed with argon and charged with different amounts of gaseous  
15 ammonia (cf. column I, Table III).

- The reactor was subsequently charged with hydrogen and at intervals hydrogen was introduced to bring the pressure up to 500 kPa. The progress of the hydrogenation reaction was followed on the basis  
20 of the hydrogen uptake as indicated by the manometer. At regular intervals samples were taken to determine the fatty acid composition and the transisomer content, as expressed in Table III. The fatty acid composition at 2% C18:3 was determined by interpolation.

25

TABLE III

Amount of ammonia added (mmol)	Hydrogenation time (min.)	Fatty acid composition (mol.%)					Trans (mol.%)
		C16:0	C18:0	C18:1	C18:2	C18:3	
30	Starting oil	10.6	4.0	23.0	53.0	7.0	<1
	None	16	10.5	9.0	43.6	33.3	2.0
	50	35	10.5	4.8	37.9	43.3	2.0
	100	40	10.6	4.0	35.1	46.8	2.0
	200	46	10.6	4.2	32.7	49.1	2.0
35	300	43	10.5	4.2	30.8	51.0	2.0
	400	59	10.6	4.0	30.5	51.5	2.0

Example 4

Example 3 was repeated, with the exception that no solvent was used and that the reaction temperature was 30°C. The autoclave was charged with 500 ml of soyabean oil. The fatty acid composition and the trans isomer content at 2°C C18:3 is indicated in Table IV.

TABLE IV

Amount of ammonia added (mmol.)	Hydrogenation time (min.)	Fatty acid composition (mol.%)					Trans (mol.%)
		C16:0	C18:0	C18:1	C18:2	C18:3	
None 300	Starting oil	10.6	4.0	23.0	53.0	7.0	< 1
	43	10.6	6.5	43.5	35.5	2.0	9
	35	10.5	4.0	33.0	48.5	2.0	8

Example 5

Example 3 was repeated, with the exception that the reaction temperature was 60°C. The results are given in Table V.

TABLE V

Amount of ammonia added (mmol.)	Hydrogenation time (min.)	Fatty acid composition (mol.%)					Trans (mol.%)
		C16:0	C18:0	C18:1	C18:2	C18:3	
None 300	Starting oil	10.6	4.0	23.0	53.0	7.0	< 1
	26	10.5	5.3	44.0	36.7	2.0	14
	33	10.6	4.1	34.1	47.8	2.0	11

Example 6

Example 3 was repeated, with the exception that rapeseed oil was hydrogenated at a temperature of 25°C, and that 200 mg Pd/kg oil were used.

The results are given in Table VI.

TABLE VI

Amount of ammonia added (mmol.)	Hydrogenation time (min.)	Fatty acid composition (mol.%)					Trans (mol.%)
		C16:0	C18:0	C18:1	C18:2	C18:3	
	Starting oil	4.4	1.4	54.0	21.7	12.1	< 1
None	14	4.4	7.7	64.9	14.6	2.0	9
400	107	4.4	1.7	60.2	25.3	2.0	11

Example 7

The hydrogenation of soyabean oil was carried out at a pressure of up to 1000 kPa using platinum as a catalyst at 20°C in an autoclave of 0.3 dm<sup>3</sup> volume, which was provided with an inlet for gases, a manometer, a stirrer and a sampling device.

The reactor was charged with 200 mg of a 5% platinum-on-carbon catalyst, 25 ml soyabean oil and 75 ml hexane. The autoclave was degassed two or three times, flushed with nitrogen and charged with gaseous ammonia.

The reactor was subsequently charged with hydrogen. The progress of the hydrogenation was followed on the basis of the hydrogen uptake as indicated by the manometer. At regular intervals samples were taken to determine the fatty acid composition and the trans isomer content, as expressed in Table VII.

TABLE VII

Amount of ammonia added (mmol.)	Hydrogenation time (min.)	Fatty acid composition (mol.%)					Trans (mol.%)
		C16:0	C18:0	C18:1	C18:2	C18:3	
	Starting oil	10.7	4.0	25.3	53.1	6.7	< 1
20 {	45	10.7	5.3	31.7	48.1	4.1	< 1
	90	10.6	6.1	37.9	43.1	2.2	< 1
	130	10.7	7.6	45.8	39.9	0.9	< 1

Example 8

Example 7 was repeated, with the exception that as the catalyst 400 mg of a 5% rhodium-on-carbon catalyst was used.

- 5 The fatty acid composition at 2% C18:3 after hydrogenation was:  
10.6% C16:0, 7.6% C18:0, 41.6% C18:1, 38.0% C18:2. The hydrogenation  
time was 270 minutes.


- 10 A similar hydrogenation without the addition of ammonia was carried  
out in the glass reactor of Example 1 using a hydrogen pressure of  
100 kPa and 120 mg of the 5% rhodium-on-carbon catalyst.

At 2% C18:3 the fatty acid composition was:

- 15 10.5% C16:0, 19.8% C18:0, 34.7% C18:1 and 32% C18:2.

The hydrogenation time was 72 minutes.

C L A I M S

1. Process for the selective hydrogenation of unsaturated fatty acid derivatives which contain besides fatty acids with two double bonds fatty acids with more than two double bonds, in the presence of a catalytically active metal of group VIII of the periodic system  
5 of elements which as a promotor can contain a metal of the same or another group of the periodic system, and has been treated with a nitrogen compound, characterized in that as the catalytically active metal palladium, platinum, rhodium or iridium is used that has been treated with dry ammonia, in a molar ratio of ammonia to  
10 metal of at least 100:1, and the hydrogenation is carried out at a temperature ranging from  $-20^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ .
  2. Process according to claim 1, characterized in that the catalyst is pre-treated with gaseous or liquid ammonia.  
15
  3. Process according to claim 1 or 2, characterized in that, before the hydrogenation is started, gaseous or liquid ammonia is added to a suspension of the catalyst.
  - 20 4. Process according to claim 3, characterized in that during the addition of the ammonia, the catalyst is suspended in the substrate to be hydrogenated.
  5. Process according to claim 3, characterized in that during  
25 the addition of the ammonia, the catalyst is suspended in an organic solvent.
  6. Process according to claim 5, characterized in that the catalyst is separated after the treatment with the ammonia and is  
30 subsequently added to the substrate to be hydrogenated.
  7. Process according to claim 3, characterized in that during the addition of the ammonia, the catalyst is suspended in a solution of the substrate to be hydrogenated in an organic solvent.  
35
  8. Process according to claims 1-7, characterized in that the hydrogen gas used for the hydrogenation contains ammonia.
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9. Process according to claims 1-8, characterized in that the hydrogenation is carried out at a temperature of  $0^{\circ}$  to  $60^{\circ}\text{C}$ .
10. Process according to claims 1-9, characterized in that the  
5 substrate to be hydrogenated is an edible triglyceride oil.
11. Fatty acid derivative hydrogenated by application of a process according to claims 1-10.



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European Patent  
Office

## EUROPEAN SEARCH REPORT

Application number

EP 80 20 0577

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D	BE - A - 872 476 (LABOFINA S.A.) * Page 3, paragraphs 2-5; page 4, paragraphs 2,3; page 5, paragraph 3; example 1V *	1-3,5, 6,9-11	C 11 C 3/12 B 01 J 23/40
P	GB - A - 2 019 309 (UNILEVER LTD.) * Page 1, line 118 - page 2, line 121 *	1,4,9- 11	
A	BE - A - 851 202 (JOHNSON, MATTHEY & CO.)		TECHNICAL FIELDS SEARCHED (Int. Cl.)  C 11 C 3/12 B 01 J 23/40 23/42 23/44 23/46 C 01 B 7/00
			CATEGORY OF CITED DOCUMENTS  X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search  The Hague		Date of completion of the search  25-09-1980	Examiner  SCHUERMANS